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Studies of interaction between He and elements with mass number 140 in Fe by time-differential perturbed-angular-correlation measurements

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Abstract

Room-temperature time-differential perturbed-angular-correlation (TDPAC) spectra of ^{140}Ce arising through ^{140}Ba - ^{140}La from ^{140}Cs in He-doped Fe, unannealed and annealed in vacuum at various temperatures, were taken in order to examine whether Ce (or rather, La and Ba) and He form complexes having a definite geometrical structure in Fe as suggested in first-principles density functional theory calculations. No clear signal of such complexes was observed in the TDPAC spectra. However, the TDPAC spectra indicate that Ce and He form complexes having a variety of geometrical structures. Comparison with reported TDPAC results on ^{111}Cd arising from ^{111}In in He-doped stainless steel shows that the parent atoms (La and Ba) of ^{140}Ce trap He atoms more efficiently than In atoms do, indicating stronger bonding of He to the former atoms, while different from the present case, ^{111}Cd (In)-He complexes form a unique geometrical structure.

Keywords: He, Ce, ion implantation, Fe, defects

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1. Introduction

Understanding of the behavior of He atoms in metals, especially in Fe, is one of important research subjects in materials science related to nuclear fusion reactor materials. Recently, Hao and Geng predicted from their first-principles density functional theory calculations that in bcc Fe, Ce has a stronger attraction to He (-1.31 eV/atom pair) than He does to another He (-1.18 eV/atom pair) and as a result a local structure is formed by a tetrahedron Ce cage encapsulating a He atom, suggesting that Ce, La with an electronic structure similar to Ce, and possibly some other rare earth elements could pin down mobile He atoms and thereby impede the He bubble growth supposedly produced in steel making up a fusion reactor [1].

This time, we have taken room-temperature TDPAC (time-differential perturbed-angular-correlation) spectra of ^{140}Ce in He-doped Fe, unannealed and annealed in vacuum at various temperatures, in order to examine whether Ce (or rather, La and Ba, which are parent atoms of ^{140}Ce) and He form complexes in Fe, applying the result [2] that we observed a unique magnetic hyperfine interaction at the 2083-keV state of ^{140}Ce (a nuclear spin $I = 4$ and a half-life $t_{1/2} = 3.4$ ns) in Fe. The TDPAC method is a nuclear spectroscopic technique, which provides local information in matter through hyperfine interactions between radioactive probe nuclei and the surrounding polarized spins and charge distribution giving electric field gradients (EFGs) [3, 4]. The TDPAC method has been applied to studies on defects [5]. If a local structure as suggested in [1] is formed with Ce (and the parent atoms of ^{140}Ce) and He in Fe, a characteristic pattern is expected to appear in the TDPAC spectra, which reflects hyperfine magnetic interactions different from (probably smaller than) the one observed in [2] and also electric quadrupole interactions. The TDPAC spectra are also compared with reported TDPAC results on ^{111}Cd arising from ^{111}In in He-doped stainless steel [6], in which latter case a clear signal was observed of the formation of ^{111}Cd (or rather In)-He complexes having a definite geometrical structure.

2. Experimental procedures

Since neither La nor Ce forms a solid solution with Fe, room-temperature implantation of ^{140}Cs ions was performed at the solid-state physics beam course of the online isotope separator at the Kyoto University reactor (KUR-ISOL) [7]. These ^{140}Cs ions were obtained by the fission reaction of a 50-mg ^{235}U target with thermal neutrons of $3 \times 10^{12}/\text{cm}^2\cdot\text{s}$ and were carried to the surface ionizer

by PbI_2 aerosol in a mixed gas jet of He and N_2 . The ionized fission products were accelerated to 30 keV for mass analysis. Mass-separated ^{140}Cs ions were further accelerated to 100 keV by the post accelerator, successively decaying through ^{140}Ba and then ^{140}La into ^{140}Ce as shown in Figure 1 [8]. Three samples were prepared using one and same Fe foil. The Fe foil was of size $10\text{ mm} \times 10\text{ mm} \times 0.1\text{ mm}$ and of 99.995% purity, annealed in H_2 atmosphere at 973 K for 2 h and then electropolished. Assuming the situation that rare earth atoms predoped in an Fe matrix pin down mobile He atoms projected from the outside of the Fe, mentioned in Introduction, or from the inside via, for example, the (n, α) reaction, the first sample was prepared by projecting about 1.4×10^{12} $^{140}\text{Cs}^+$ into an area of 0.2 cm^2 , followed by He^+ implantation at room temperature with a dose of about $4 \times 10^{13}/\text{cm}^2$. We name this sample He-doped(1) $^{140}\text{CeFe}$. The second and third samples were prepared by projecting about $5 \times 10^{14}/\text{cm}^2$, and about $2 \times 10^{16}/\text{cm}^2$ He^+ in this order on the first sample. We designate these samples He-doped(2) $^{140}\text{CeFe}$ and He-doped(3) $^{140}\text{CeFe}$, respectively (the number in the parentheses stands for the number of He irradiations). The implantation of He was carried out at room temperature in vacuum of $8 \times 10^{-6}\text{ Pa}$ using an ion beam gun manufactured by Omegatron Co., in which mono-energetic 4-keV He^+ ions were collimated and mass-analyzed [9]. Figure 2 shows that the concentration profile of He in Fe overlaps that of ^{140}Cs , both of which were calculated with a SRIM code [10].

For the He-doped(3) $^{140}\text{CeFe}$ sample, 30-min annealing in vacuum ($\sim 1 \times 10^{-4}\text{ Pa}$) was performed at 473 K, 673 K, 873 K, 973 K, and 1073 K in this order. After each annealing, no radioactivity loss from the samples was noticed.

The time dependences of the coincidence counts $N(\theta, t)$ of the 329-487 keV cascade γ rays for the three Fe samples were taken at room temperature with a measurement system, consisting of standard fast-slow electronic modules and four BaF_2 scintillation detectors. Here, θ and t denote the angle and the time interval, respectively, between the cascade γ rays. The directional anisotropy $A_{22}G_{22}(t)$, which we call the TDPAC spectrum, is obtained as follows:

$$A_{22}G_{22}(t) = 2 \frac{N(180^\circ, t) - N(90^\circ, t)}{N(180^\circ, t) + 2N(90^\circ, t)}. \quad (1)$$

The $10\text{ mm} \times 10\text{ mm}$ irradiation plane of the Fe foil was set parallel to the detector plane. The distance between the center of the source and the head of each BaF_2 detector was 3.0 cm. With

four detectors, slight differences in γ -ray detection efficiency among the detectors are eliminated in the operation of equation (1) [2].

The coefficient A_{22} depends only on the nuclear transitions and its value for ^{140}Ce is reported to be -0.13 [11]. The perturbation factor $G_{22}(t)$ for an ensemble of randomly oriented microcrystals is a function of the Larmor frequency ω_L for a unique static magnetic interaction. The quantity ω_L is defined as usual: $\omega_L = -\mu B/\hbar$, where μ is the magnetic moment and B is the magnetic field at the nucleus. In the 180° - 90° angular correlation case with no external magnetic field,

$$A_{22}G_{22}(t) = A_{22} [1 + 2\cos(\omega_L t) + 2\cos(2\omega_L t)]/5, \quad (2)$$

having the constant term (which we call the baseline in the text) of $A_{22}/5$.

All the TDPAC measurements including a measurement on the Fe sample before the first He implantation were done more than about a week after the end of the ^{140}Cs bombardment so that the number ratio of ^{140}La to ^{140}Ba always equals $t_{1/2}(^{140}\text{La})/[t_{1/2}(^{140}\text{Ba}) - t_{1/2}(^{140}\text{La})] = 0.15$ during the TDPAC measurements and also the three He irradiations, where $t_{1/2}(^{140}\text{La}) = 40.3$ h and $t_{1/2}(^{140}\text{Ba}) = 12.8$ d.

3. Results and discussion

Figure 3 (from top to bottom) depicts the TDPAC spectra obtained at room temperature for $^{140}\text{CeFe}$ ($\sim 1.4 \times 10^{12}/0.2 \text{ cm}^2$ ^{140}Cs) before He irradiation, He-doped(1) $^{140}\text{CeFe}$ ($\sim 4 \times 10^{13}/\text{cm}^2$ He), He-doped(2) $^{140}\text{CeFe}$ ($\sim 5 \times 10^{14}/\text{cm}^2$), and He-doped(3) $^{140}\text{CeFe}$ ($\sim 2 \times 10^{16}/\text{cm}^2$), all four with no annealing, and for He-doped(3) $^{140}\text{CeFe}$ annealed at 673 K, 873 K, and 1073 K. The top spectrum in Figure 3 is the one appearing in [2]. As explained there, the oscillation pattern seen in the spectrum is due to a unique static magnetic hyperfine interaction at ^{140}Ce occupying the Fe substitutional site with no lattice defects nearby (the Larmor frequency ω_L equals $1.927(7)$

Grad/s).¹ These ^{140}Ce experience no electric quadrupole interaction and are in the diamagnetic Ce^{4+} state (no 4f electron). Hereafter, we call these ^{140}Ce "good" ^{140}Ce . Because the amplitude of the oscillation is $-0.042(3)$, while the reported A_{22} value is -0.13 , "good" ^{140}Ce are only about 30% of the ^{140}Ce implanted in Fe. This value of 30% agrees with the fraction of Ce assigned to those occupying the substitutional Fe site, 28.9(5)%, which was in turn obtained in a nuclear orientation experiment on ^{141}Ce in Fe, where 115 keV ^{141}Ce ions were directly implanted in Fe with a dose of less than $3 \times 10^{12}/\text{cm}^2$ [12], while in our case 100 keV ^{140}Cs ions (decaying to ^{140}Ce through ^{140}Ba and then ^{140}La) were implanted in Fe with a dose of $\sim 1.4 \times 10^{12}/0.2 \text{ cm}^2$.

In addition to the oscillation component, there are other components in the TDPAC spectrum corresponding to the remaining 70% of the ^{140}Ce implanted in Fe. Noting that the baseline of the TDPAC spectrum is nearly equal to $A_{22}/5$ ($= -0.026$), which is the first term of equation (2), these components are judged due to static perturbations.² Considering that there are events in which atomic vacancies produced during the ^{140}Cs irradiation move and bond to ^{140}Cs ($t_{1/2} = 63.7 \text{ s}$) and possibly ^{140}Ba , these components arise from those ^{140}Ce at the Fe sites having vacancies nearby, or at interstitial sites, or in grain boundaries, feeling a variety of static hyperfine magnetic fields and EFGs such that the oscillations arising from these variety of fields interfere among themselves and get damped quickly in the TDPAC spectrum.

In Figure 3 are also shown the characteristic values for each oscillation component seen in the TDPAC spectra, which were obtained by fitting equation (2) taking account of the time resolution of the measurement system. As the dose of He increases to about $5 \times 10^{14}/\text{cm}^2$, the oscillation amplitude gets reduced more and more (note that the amplitude is not damped with time), and at the dose of about $2 \times 10^{16}/\text{cm}^2$ (He-doped(3) $^{140}\text{CeFe}$) no clear oscillation is observed. According to the calculation of the SRIM code used in making Figure 2, the dose of 2

¹ Although according to equation (2) in the text, there should be two frequency components for one magnetic interaction, there seems to be only one frequency component for the oscillation pattern. This is due to the finite time resolution of the present detection system, 1 ns, about 10 times larger than the time bin of the time spectra. The third term of equation (2) that is proportional to $\cos(2\omega_L t)$ is almost averaged out.

² In the case of a dynamic perturbation, $G_{22}(t)$ exponentially decreases to zero with increasing t .

$\times 10^{16}/\text{cm}^2$ corresponds to 0.15 dpa (displacement per atom) at the maximum. This large number may imply that He ions directly displace the parent atoms of "good" ^{140}Ce from the substitutional sites. However, based on the fact that the oscillation amplitude is reduced by as much as about 50% even for the He-doped(1) $^{140}\text{CeFe}$ ($\sim 4 \times 10^{13}/\text{cm}^2$ He corresponding to only 0.0003 dpa), it is unlikely for He ions to directly displace them. We think that He atoms diffused and bonded to the parent atoms of "good" ^{140}Ce , since interstitial He atoms (a calculated activation energy is 0.06 eV [13]) diffuse much more easily than vacancies (a calculated activation energy is 0.68 eV [14]). As the dose of He increases, the number of the parent atoms of "good" ^{140}Ce decreases. If ^{140}Ce -He complexes take one or a few definite geometrical structures, these would be reflected in the TDPAC spectra and it may be possible to determine whether He atoms are at substitutional or interstitial sites. The observation that the oscillation amplitude is only reduced but not damped with time under the He implantation indicates that ^{140}Ce -He complexes take a variety of geometrical structures, accordingly these ^{140}Ce bonded by He feeling various EFGs due to He. It is natural to think that many He atoms surround the parent atom and that there is a distribution of the number of He atoms attached to it. With annealing at higher temperature, the TDPAC pattern changes and we thus suppose that still more He atoms that are released from He-vacancy clusters and possibly vacancies bond to already formed complexes of the parent atoms of ^{140}Ce and He atoms. In the present doping process, Ce (and the parent atoms)-He complexes were not formed which have any definite local structure including that as suggested in [1], a tetrahedron Ce cage encapsulating a He atom in an Fe matrix, for which structure this may be a matter of course, since the number of Ce is 4 times larger than that of He, while the dose of ^{140}Cs leading to ^{140}Ce is much smaller than that of He.

Let us contrast our TDPAC results with those obtained by Deicher *et al.* on the 245-keV state of ^{111}Cd ($I = 5/2$ and $t_{1/2} = 85$ ns) arising from ^{111}In in He-doped stainless steel [6]. As one of several samples for their TDPAC measurements, they prepared a stainless steel sample implanted with 350 keV $^{111}\text{In}^+$ ($\sim 3 \times 10^{11}/0.2 \text{ cm}^2$) and then 15 keV He^+ ($\sim 1 \times 10^{16}/\text{cm}^2$). Like our case, the distributions of 350 keV ^{111}In and of 15 keV He^+ overlap each other, although these average depths are about 3 times larger than our case. They observed a unique electric quadrupole interaction: the quadrupole frequency ω_Q equals 37.7(8) Mrad/s and the asymmetry parameter η 0.15(5). Here, ω_Q is defined as $eQV_{zz}/[4I(4I - 1)\hbar]$ and η as $(V_{xx} - V_{yy})/V_{zz}$, where e stands for

elementary electric charge, Q nuclear quadrupole moment, and V_{xx} , V_{yy} , and V_{zz} the principal components of EFG tensor satisfying the condition that $|V_{xx}| \leq |V_{yy}| \leq |V_{zz}|$. When we correct V_{zz} using the values of the antishielding factor for Cd and Ce [15], the ω_Q value for ^{140}Ce would be 14 Mrad/s and such a ω_Q value would be easily identified in the present TDPAC spectra even if electric quadrupole interaction is combined with magnetic hyperfine interaction. Different from our case, it was concluded that a few He atoms bond to an In atom (the parent atom of ^{111}Cd).

Deicher *et al.* derived the annealing temperature dependence of the fraction, which they named f_2 , of the He- $^{111}\text{Cd}(\text{In})$ complex component (each annealing was done for 10 min in vacuum of 1×10^{-3} Pa or less): f_2 is only about 12% at room temperature (i.e., no annealing), increases slowly up to about 25% at 723 K, then increases rapidly up to as much as about 90% at 923 K, turns to decreasing there, and becomes about 80% at 1073 K, where the In atoms start to diffuse out of the steel matrix. As described above, the oscillation in the TDPAC spectrum is attenuated by as much as about 50% even for the He-doped(1) $^{140}\text{CeFe}$ ($\sim 4 \times 10^{13}/\text{cm}^2$ He and no annealing), meaning that about 50% of "good ^{140}Ce " changed to ^{140}Ce -He complexes under the He dose being about 100 times smaller than the case for $^{111}\text{Cd}(\leftarrow ^{111}\text{In})$. We thus conclude that the parent atoms of ^{140}Ce (La and Ba) trap He atoms more effectively than In atoms do.

4. Conclusions

In order to examine whether Ce and He form complexes having a definite geometrical structure in Fe as suggested in first-principles density functional theory calculations, we irradiated at room temperature an Fe foil first with 100-keV ^{140}Cs ($\sim 1.4 \times 10^{12}/0.2 \text{ cm}^2$) and then with 4-keV He having three different doses ($\sim 4 \times 10^{13}/\text{cm}^2$, $\sim 5 \times 10^{14}/\text{cm}^2$, and $\sim 2 \times 10^{16}/\text{cm}^2$) and took room-temperature TDPAC spectra of ^{140}Ce arising from ^{140}Cs . We also performed isochronal annealing on the Fe foil after the He implantation of $\sim 2 \times 10^{16}/\text{cm}^2$ and took room-temperature TDPAC spectra of ^{140}Ce . The TDPAC spectra indicate that Ce (and the parent atoms of ^{140}Ce) and He form complexes but these complexes do not have a definite geometrical structure. This is contrasted with the case of the 245-keV state of ^{111}Cd ($I = 5/2$, $t_{1/2} = 85 \text{ ns}$) arising from ^{111}In in He-doped stainless steel. We conclude that Ce (and the parent atoms of ^{140}Ce) form complexes with He having a variety of geometrical structures, the number of He atoms attached to Ce (and

the parent atoms of ^{140}Ce) being rather large, and that the parent atoms trap He atoms more efficiently than In atoms do.

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Figure Captions

Figure 1. Simplified decay scheme of the relevant $A = 140$ mass chain.

Figure 2. Distributions of 100-keV ^{140}Cs (●) and 4-keV He (○) in Fe. Note that in the actual irradiations, the number of ^{140}Cs is much smaller than that for He.

Figure 3. Room-temperature TDPAC spectra for $^{140}\text{CeFe}$ ($\sim 1.4 \times 10^{12}/0.2 \text{ cm}^2$ ^{140}Cs) before He irradiation, He-doped(1) $^{140}\text{CeFe}$ ($\sim 4 \times 10^{13}/\text{cm}^2$ He), He-doped(2) $^{140}\text{CeFe}$ ($\sim 5 \times 10^{14}/\text{cm}^2$ He), and He-doped(3) $^{140}\text{CeFe}$ ($\sim 2 \times 10^{16}/\text{cm}^2$ He), all with no annealing, and He-doped(3) $^{140}\text{CeFe}$ annealed at 673 K, 873 K, and 1073 K in vacuum. The two values in the square brackets in each panel are the Larmor frequency in units of Grad/s and the amplitude of the oscillation component, obtained by fitting equation (2) in the text to the spectrum taking into account the finite time resolution of the measurement system. The number in each parenthesis in the top panel is the uncertainty attached to the last digit of the value of the relevant quantity. The same uncertainties are applied to the other cases.

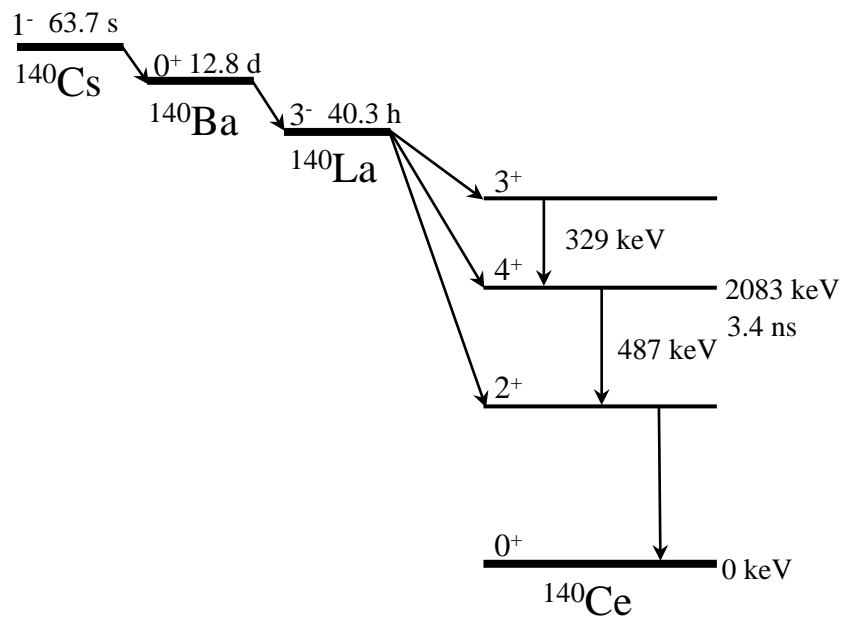


Figure 1 Y. Ohkubo et al.

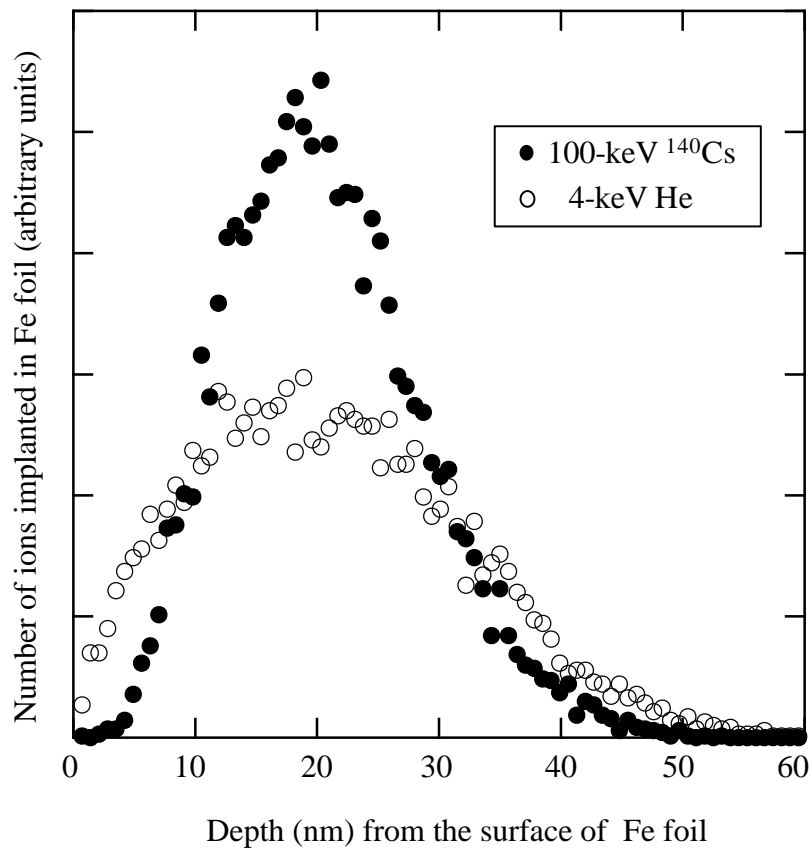


Figure 2 Y. Ohkubo et al.

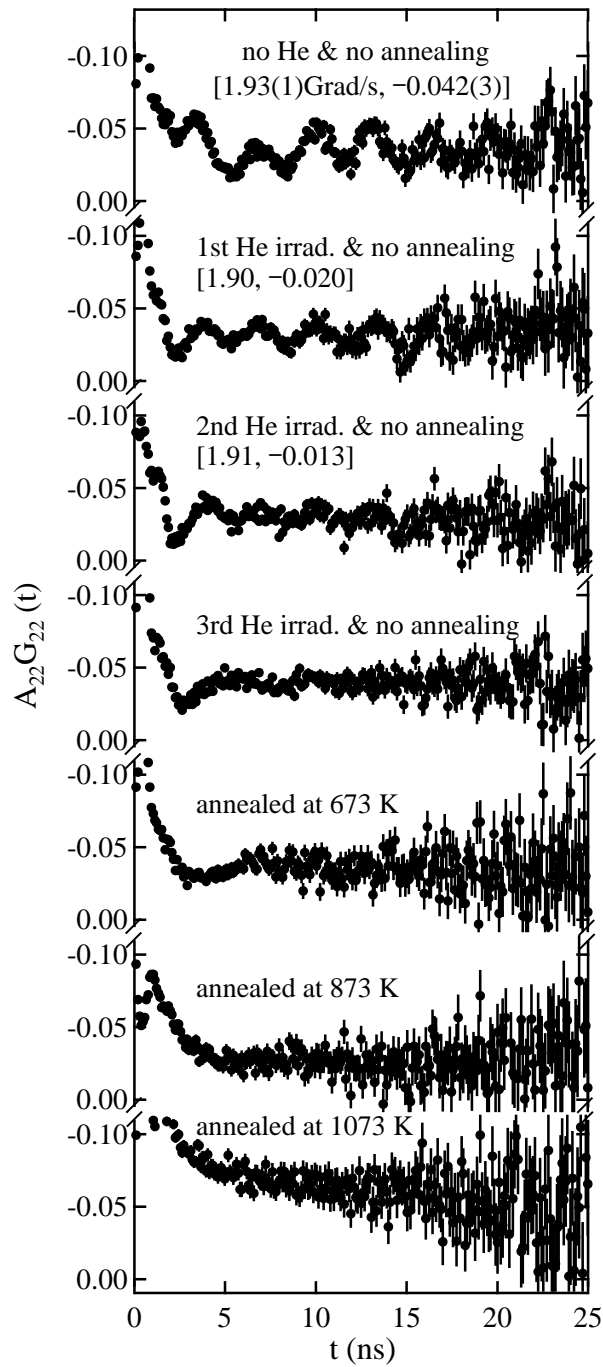


Figure 3 Y. Ohkubo et al.